N_2O_5, Reservoir Species and Stratospheric Ozone

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Over the last decade, advances in theoretical numerical models of the atmosphere have resulted in the recognition of a significant number of trace constituents as being important in explaining chemistry relevant to the stratospheric ozone distribution. Unfortunately, primarily due to difficulties in achieving enough measurement sensitivity, the stratospheric concentrations of many of these species, particularly those termed 'reservoir' species, have, until recently, remain unobserved. Reservoir species are those trace constituents, such as HNO_3, HCl, N_2O_5, $ClONO_2$, and others, that are produced from the more reactive ozone destroying species, but are longer-lived and less reactive. In a sense, these gases act as temporary reservoirs or holding tanks for the more reactive ozone-destroying forms of nitrogen-, chlorine-, and hydrogen-containing species in the stratosphere. Of these reservoir species, only HNO_3 and HCl have been measured extensively. In this issue of Nature, Toon et al.[1] report the first conclusive measurement of the reservoir species N_2O_5. Their observed concentration distribution applies only to a particular latitude and longitude on a single day, but nonetheless represents an important step toward the validation of key aspects in the theory of ozone controlling mechanisms.

Many recent studies have concerned the possibility that currently increasing concentrations of human-influenced emissions of trace gases, such as methane (CH_4), nitrous oxide (N_2O), and chlorocarbons (particularly the industrially produced $CFCl_3$ and CF_2Cl_2) may be affecting the distribution of stratospheric ozone. These trace gases, although emitted at the earth's surface are sufficiently long-lived that they are transported to the upper atmosphere, where they are dissociated and their by-products can react with ozone catalytically. The rate of conversion of these reactive species to the less reactive, reservoir species largely determine the ultimate effect that trace gases may have on stratospheric ozone. Historically, it has been noted that model-derived concentrations of the reservoir species have been particularly sensitive to remaining uncertainties in atmospheric chemical reaction rates. Because of these reasons, measurements of the reservoir species concentrations in the stratosphere have been deemed a vital priority.

Measurements of N_2O_5 concentrations are of particular interest for several reasons. N_2O_5 has long been theorized to play an important role in the diurnal variation of NO_2, which in turn is an important reactant with ozone. The slow photolysis of N_2O_5 should slowly produce NO_2 during the day, while production of N_2O_5 should slowly reduce NO_2 concentrations in the night-time stratosphere. Observations of the sunrise-sunset differences in the NO_2 profile[2,3] and a recent analysis[4] of satellite observed NO_2 at varying zenith angles have tended to verify the importance of this process. The observations by Toon et al. are in general compatability with the expected diurnal behavior of N_2O_5.

Model calculations have suggested that N_2O_5 concentrations should be particularly large in the high latitude winter, especially in the Arctic. In fact, calculations suggest that N_2O_5 may be the major portion of total reactive nitrogen in the high latitude stratosphere. Trajectory analyses[5] suggest that the conversion of NO_2 to N_2O_5 in the winter polar night may explain the so-called Noxon cliff, in which sharp gradients in the total vertical column content of NO_2 have been observed at high latitudes. Measurements of N_2O_5 concentrations in the polar winter stratosphere in tandem with further observations of NO_2 concentrations are needed to test this. In addition, heterogeneous mechanisms[6] have been proposed for the conversion of N_2O_5 to HNO_3 in the arctic winter. This can also be tested through N_2O_5 observations in this region.

The observed profile of N_2O_5 in Toon et al. is in general agreement with the expected theoretical distributions determined with models such as our 1-D model at LLNL, but a direct comparison would depend on knowing observed NO_2 and O_3 concentrations at the same location. It would be desirable to develop a refined measurement technique that would not be as dependent on an assumed profile shape as the existing measurements by Toon et al are. The figure below shows the latitudinal variation in N_2O_5 concentrations determined for May at local noon from the model of S. Solomon and R. Garcia. Obviously, from this (and other results which show the strong winter high latitude gradients), observations of N_2O_5 are needed at a wide range of seasons and locations, as well as time of day, to validate theory.

1. Toon, G. C., C. B. Farmer, and R. H. Horton, Nature, this issue, 1986.

2. Noxon, J. F., E. C. Whipple, and R. S. Hyde, J. Geophys. Res. 84, 5047.

3. Kerr, J. B., C. T. McElroy, and W. R. J. Evans, Can. J. Phys., 60, 196, 1982.

4. Solomon, S., and J. M. Russell, J. Geophys, Res., in press, 1986.

5. Solomon, S., and R. Garcia, J. Geophys. Res. 88, 5497, 1983.

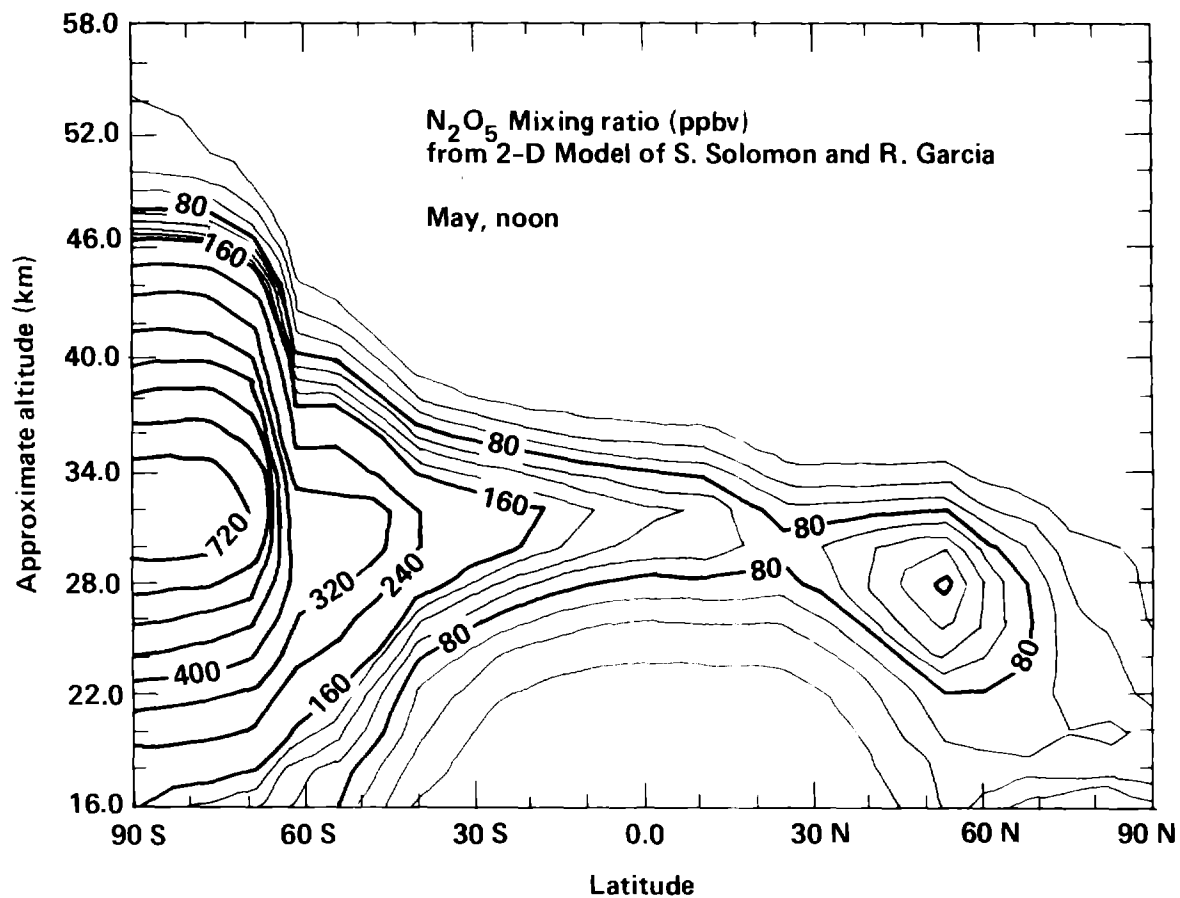6. Evans, W.F.J., C.T. McElroy and I.E. Galbally, Geophs. Res. Lett. 12, 825, 1985.

Figure 1. Calculated global variations in N_2O_5 mixing ratio for May at local noon as derived from the two dimensional model of S. Solomon and R. Garcia. By definition, mixing ratio is the concentration divided by the air density, while ppbv means parts per billion by volume.